

Atomic-Resolution Electron Energy Loss Spectroscopy in the Scanning Transmission Electron Microscope: Understanding the Limits to Scaling Nano-Transistors

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The smallest feature on the transistors used in computer circuits is the gate oxide. In early 1999, a typical SiO₂ gate oxide was about 14 oxygen atoms thick. In early 2000, the oxide thickness had shrunk to 8 oxygen atoms. Between 2003 and 2008, the projected gate oxide thickness will be 4 oxygen atoms (1 nm). It is now technologically possible to produce nano-transistors with 5 oxygen-atom-thick gate oxides and 35 nm channel lengths[1]. However when the gate thickness is reduced to 4 oxygen atoms, the device performance is dramatically degraded. Using atomic-scale electron energy loss spectroscopy (EELS)[2] and ab-initio electronic structure calculations, we have shown that the *electrical* transition region from Si to SiO₂ occurs over a region that is 0.3-0.4 nm wide, even when the *structural* transition is atomically abrupt. The spectroscopy is performed in a scanning transmission electron microscope where Electrons scattered through a thin, cross-sectioned sample undergo energy losses characteristic of the different elements in the sample and their local environment. By scanning the electron beam across an interface and recording energy loss spectra at each point in the scan, a composition and electronic-structure profile can be built up, atom-column by atom-column.

A local-moments analysis shows the magnitude of local bandgap is proportional to the number of O 2nd nearest neighbors around a given O atom, and the bulk SiO₂ gap is only obtained for a fully coordinated 2nd neighbor shell. This puts a fundamental limit of 0.7 nm on the oxide thickness in order for the bulk SiO₂ barrier height to be achieved. SiO₂ films thinner than this will not exhibit the bulk dielectric constant or barrier height. Interface roughness increases the minimum usable thickness for present growth techniques and severely impacts the performance of transistors using gate dielectrics with effective oxide thicknesses less than 1.3 nm. As most replacement gate dielectrics contain subnanometer-thick silicon oxide layers, similar physical constraints apply. EELS analysis has proved very useful in identifying promising alternative materials.

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Electron back-scattering contribution to the electron emission anisotropy by keV range electron beams*

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The dependence of the electron-excited Auger emission by the incidence direction (PDMEE, or Primary-beam Diffraction Modulated Electron Emission [1]) can be exploited to obtain information about the crystal structure in the near-surface region. As far as adsorbates or ultra-thin hetero-epitaxial layers are concerned, the interpretation of the intensity distribution curves is not straightforward due to the superposition of true overlayer focusing-diffraction effects and back-scattering of the beam electrons by the substrate atoms [2-4]. Since the former effect ends in quite small modulations of the Auger signal (almost zero if no overlayer-overlayer focusing is allowed), the substrate back-scattering plays a significant role in most experimental situations and often is the main source of the overlayer signal anisotropy. We proposed a multi-step mechanism that involves forward-focusing of the beam electrons in the sub-surface region and their subsequent back-scattering to the surface region to explain the anisotropy of the surface signal. In this work we systematically tested the different assumptions contained in the multi-step model both by direct measure of some of the relevant physical parameters such as the intensity and the anisotropy of the back-scattered electrons in a wide energy range and by computer modeling of the experimental conditions. Monte Carlo simulations of the electron trajectories and single-scattering cluster calculations helped to get information about the physical quantities which are not directly accessible by experiments. The relationship between the angular anisotropy of the surface signal and the surface structure itself is also discussed.

* Work supported by Istituto Nazionale per la Fisica della Materia

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M_{4,5} Resonant Raman Scattering with final $4p$ - $4d$ holes in Te, La and Gd: trends of the many body effects*

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Configuration Interaction (CI) between the single $4p$ hole and the double $4d$ hole configurations is studied in elemental Te, La and Gd by soft X-ray Resonant Raman Scattering (RRS) with excitation at the M₅ and M₄ absorption edges. The ($4p^{-1}$ - $4d^2$) CI is a typical example of many-body effect where the one electron picture breaks down completely as it has been already observed many years ago [1]. RRS technique has been recently demonstrated to be able to address this final state interaction problem in a cleaner and more selective way than the photoemission technique already used [1], showing that also other contribution like multiplet splitting have to be taken into account [2]. This higher selectivity is now exploited to study the evolution of the CI effect in the region of the periodic table where it is non-negligible. The experimental data show a non-trivial evolution of the spectral weight of the CI and of its excitation energy dependence with the atomic number Z , whereas the spectral energy extension is nearly constant (around 50-55 eV at M₅ excitation edge) in the three cases. Comparison with first principle calculations like Cowan's Hartree-Fock code calculations has not been possible yet due to their computational complexity. Nevertheless it is shown that the trends and energy scales of the experimental data can be rationalized in a qualitative model based on important parameters of such kinds of calculations. These parameters are the energy scales of the multiplet splitting, spin-orbit and CI interactions together with the energy separation of the $4p^{-1}$ and $4d^2$ configurations. Particularly the model explains the very different sensitivity of RRS against the change from M₅ to M₄ excitation and the change in weight of the final configurations having very high excitation energies in the three cases.

* Work supported by the INFN, Italy, and the ESRF, France, under the AXES project agreement.

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New Application of the Multiplet Theory: Calculation of the Electric Quadrupole and Dipole transitions in the K Pre-Edge Features of Fe and Cr ions - Multielectronic and Crystal Field Effects and Hybridization Linear Dichroism

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The pre-edge features at the K edges are commonly used as sensitive fingerprints of the local electronic structure of transition metal ion (site symmetry and valence). The pre-edge features are usually associated with electronic transitions from the 1s core orbital to the localized 3d orbitals (electric quadrupole transitions) and to the 4p orbitals mixed to the 3d (electric dipole transitions). They strongly depend on the local symmetry which affect the degree of admixture between 4p and 3d orbitals.

Multiplet theory has been applied to the calculation of the $L_{2,3}$ edges of transition metal ions, involving 3d levels ([1] and references therein). Since 3d levels are involved in the K pre-edge features, we applied the Multiplet theory to the calculation of the electric dipole and quadrupole transitions. We show that the Multiplet model can be used to extract local structure parameters of transition metal ions, such as crystal field strength (10Dq), Racah parameters i.e. electronic repulsion intensities and the degree of admixture between 3d and 4p levels. The method can thus be complementary to mono-electronic theories (band structure, multiple scattering, finite differences), which are commonly applied to the calculation of the K edges and pre-edges ([2] and references therein) but have not access to these parameters.

Theoretical development : We present here a new model for p-d hybridization which occurs in noncentrosymmetric sites like tetrahedral sites. For the first time, the absolute intensities of the electric dipole and the quadrupole transitions are obtained in the Ligand Field Multiplet approach, thus quadrupole to dipole intensities ratio are determined. Since the dipole intensity is directly related to the p-d hybridization, information on the bonding characteristics and the local electronic structure can be derived from this model.

Applications : The calculations are applied to the case of K pre-edge features of Fe^{2+} and Fe^{3+} ions in octahedral and tetrahedral symmetries in iron oxides. Local structure parameters are derived such as crystal field strength (10Dq), Racah parameters i.e. electronic repulsion intensities and the degree of admixture between 3d and 4p levels.

Then, we present a simulation of a natural linear dichroism experiment at the Fe and Cr K pre-edge in sapphire and ruby, which allows to study the angular dependence of the quadrupole and dipole transitions and to determine the local crystal anisotropy.

Morphology, Photoluminescence, and Electronic Structure in Oxidized Silicon Nanoclusters

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The dependence of quantum size effects on bonding structure in oxidized silicon nanoclusters is established by correlating photoluminescence data with electronic structure measurements at the Advanced Light Source. After removal from the growth chamber, our photoluminescence (PL) results indicate that as the nanoclusters oxidize, the main PL peak moves from 1.83 eV to 1.94 eV in energy. The changes in the morphology and bonding structure of the clusters was established using soft-x-ray fluorescence spectroscopy (SXF) and photon-yield near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, which probe the element-specific density of occupied (SXF) and unoccupied (NEXAFS) electronic structure. Our finding is that the as-synthesized nanoclusters consist of a pure, crystalline Si core within a nearly pure SiO₂ shell. Very few suboxides are present, and the oxidation process does not lead to an increase in the amount of suboxides present within the particles. As the nanoclusters oxidize, the radius of the crystalline core decreases in size, which gives rise to the change in the position of the PL signal.

Soft XMCD at 200 MilliKelvin: Quantum Size Effect in High Spin Paramagnetic Molecules

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The work presented here is one of the first X-Ray Magnetic Circular Dichroism experiments (XMCD) performed on paramagnetic compounds and the first in bimetallic polynuclear complexes where the molecular spin states are complex combinations of exchange-coupled local elemental spins.

High spin molecules are magnetic nanoparticles, which can behave as single-molecule magnets. They show a superparamagnetic behavior. They have original magnetic properties such as quantum size effect, quantum tunneling effect. We present here an example of quantum size effect, in the case of Prussian Blue analog high spin molecules, which has been evidenced by X-Ray Magnetic Circular Dichroism experiments ([1] and references therein).

Two compounds are chosen, based on hexacyanochromate ($\text{Cr}^{\text{III}}(\text{CN})_6$) : (i) the complex denoted $\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}_6$, with a spin $S = 15/2$ in the ground state, built through a short range ferromagnetic interaction between the central Cr^{III} ion and the six Ni^{II} ions issued from the intramolecular ferromagnetic coupling, (ii) the complex denoted $\text{Cr}^{\text{III}}\text{Mn}^{\text{II}}_6$, with a spin of $27/2$ in the ground state, built through an antiferromagnetic interaction between the central Cr^{III} ion and the six Mn^{II} ions.

XMCD measurements at the $L_{2,3}$ edges of Cr^{III} , Ni^{II} , Mn^{II} were performed at very low temperature (200mK). The experimental spectra are simulated in the Ligand Field Multiplet model. A good agreement is obtained for the isotropic absorption spectrum as well as for the dichroic signal, even in the case of strong covalent bonding such as in Cr-CN where the dichroic signal is dramatically changed as compared to a more ionic bonding. The orbital and spin magnetic moment of the different elements are derived from the calculation of the spectra (spin and orbital sum rules can not be applied in the cases of Cr^{III} and Mn^{II} where the L_3 and the L_2 edges overlap). It is shown that the strong covalency clearly modifies the magnetic moment. Moreover, these experiments at very low temperature and the calculations evidence a peculiar magnetic behavior of Cr^{III} due to the small dimension of the molecule

Theory of Magnetic Ordering and Multiplet Splitting at the Gd(0001) Surface*

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The magnetic properties of Gd(0001) are unusual, with a number of experiments finding an elevated Curie temperature at the surface, yet still some controversy over these observations and no quantitative theory as to what may be occurring. In particular, recent spin-polarized photoelectron diffraction (SPPD) experiments for epitaxial Gd/W(110) films [1] suggest a significant enhancement of the surface Curie temperature by about 85 K above the bulk Curie temperature. We here attempt to provide theoretical insight into these observations, including also new experimental results for changes in the core-level multiplet splittings observed in Gd 4s and 5s photoemission on passing through the bulk and surface transition temperatures [2]. Effects of electron correlation on the electronic structure and magnetic properties of the Gd(0001) surface are investigated using of the full-potential linearized augmented plane wave implementation of correlated band theory, often referred to as LDA+U. The correct ferromagnetic ground state for both bulk Gd and the Gd surface is obtained only with the inclusion of correlations effects via this LDA+U approach. Surface interlayer relaxation as judged from prior low energy electron diffraction studies is also found to lead to a 90 % enhancement of the interlayer surface-to-bulk effective exchange coupling, and subsequent application of a Landau-Ginzburg type theory to these results yields a 30 % enhancement of the Curie temperature at the surface, in very good agreement with the SPPD experiments. Theory also shows that the 4s- and 5s-core multiplet splittings of Gd depend on the short-range magnetic order, with the calculations providing a semi-quantitative prediction of these effects, which are in the 60 meV range.

*Supported by NSF (Grant DMR-9802076) and DOE (Contract No. DE-AC03-76F00098).

Electronic Structure of 1D Ca rows on Si(111)

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Deposition of highly reactive alkaline-earth adsorbates (Ca, Sr, Ba) onto semiconductor substrates leads to reconstructions that are inherently 1D in nature. The Ca/Si(111) system has been studied using reflection high-energy electron diffraction (RHEED), scanning-tunneling microscopy (STM), and synchrotron radiation photoemission. For Ca coverages less than 0.5 ML, a series of odd-order $n \times 1$ ($n=3,5,7,\dots$) reconstructions have been observed. The most stable of these is a (3×1) phase that occurs at 0.33 ML. Various models have been proposed for the general metal/Si(111)- (3×1) system. In this work, the accuracy of these models, as well as whether they can be altered to account for higher-order reconstructions that are observed at higher Ca coverages, is discussed. These objectives are accomplished through comparison between surface morphologies observed in STM images and the electronic structure of the different surface phases observed in high-resolution core-level and valence-band photoemission.

Photoemission Spectromicroscopy Study on Passivation of GaAs (100) by $\text{CH}_3\text{CSNH}_2/\text{NH}_4\text{OH}$

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The GaAs (100) surface etched in buffer solution of phthalate ($\text{PH}\approx 4.01$), and then passivated in $\text{CH}_3\text{CSNH}_2/\text{NH}_4\text{OH}$ solution at two different pH values were investigated using MAXIMUM Photoemission spectromicroscopy at BL12.0.1.1 at the Advanced Light Source (ALS), Berkeley. The S $L_{2,3}$ edge of NEAXFS data were also collected at Advanced Material Chamber of BL9.3.2, ALS. . The sample used in this study was single crystal GaAs (100) with doping concentration of $1\times 10^{18}/\text{cm}^2$. After regular cleaned, it was then dipped into buffer solution of phthalate ($\text{PH}\approx 4.01$) to remove the native oxides, and finally different parts of wafer were immersed into a passivation solution at 60°C for different time. There is a line marked the interface between etching and passivation before the sample inserted into UHV chamber. The morphological information, chemical states and electronic structures of the surfaces were obtained on different regions with etching and passivation on same sample. After etching and followed by passivation by $\text{CH}_3\text{CSNH}_2/\text{NH}_4\text{OH}$ solution ($\text{pH}\approx 10.0$), the sample surfaces remained smooth and mirror-like, indicating that the process of both etching and passivation are moderation. The survey spectra taken from above different regions have shown that the ratios of Ga to As are variable for the etched region and as function of passivation time, respectively. The Ga : As different ratios at different regions have implied different reactivity and solubility between solution and GaAs substrates due to different PH values. A residual of F2s level was observed at kinetic energy of 94.0eV for etched surface by the acid buffer solution, and disappeared completely after passivation in alkaline solution. The spectra of As3d and Ga3d in bulk GaAs (100) were observed for different regions, the lower kinetic energy sides both As3d and Ga3d increased gradually for passivation regions with passivation time, indicating that As_2S_3 and Ga sulfide components were formed and increased gradually. Comparing the different regions, the largest shift of Fermi level is 0.5eV toward conduction band minimum (CBM), which indicates decrease of the surface defects for the passivated surfaces.

E.D.Lu gratefully acknowledges the partial support of K.C.Wong Education Foundation, Hong Kong for his initial visiting Advanced Light Source, Lawrence Berkeley National Laboratory.

This worked is supported by the Director, Office of Science, and Office of Basic Energy Science, Advanced Light Source, of U.S. Department of Energy.

Fermi Surfaces and Magnetic Behavior of Thin FeNi Alloy Films

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We report angle-resolved and spin-resolved photoemission measurements of changes in the electronic structure with changing composition of pseudomorphic films of FeNi magnetic alloys grown epitaxially on Cu(100). With x-ray magnetic linear dichroism angle-dependent (XMLDAD) 3p core-level photoemission the evolution of the elemental magnetic moments was monitored. In addition changes occurring in the spin-polarized valence bands were observed with spin-polarized photoemission, together with changes in the k-distribution of states at the Fermi energy.

A $\langle 110 \rangle$ projection of the Fermi surface shows a delocalized "dogbone" feature due to sp-states and more localized "hotspots" corresponding to the emergence of minority spin d-states. Hybridization between the sp- and d-states occurs at these locations on the dogbone indicative to a strong nesting of wavevectors of excitations spanning the Fermi surface. The sp-dogbone states spin polarize with increasing average magnetic moment.

Both elemental moments, observed in XMLDAD, grow with increasing Fe concentration up to a maximum at the Fe concentration of 55%, that on the Fe increasing at a faster rate than the Ni moment. Beyond this point, the Fe moment shows a rapid decline to a "low-spin" value, of the order of that of the Ni moment, which tracks the behavior of the Fe moment but to a smaller degree.

Spin-resolved valence band photoemission measurements show first an increase in the exchange splitting of the 3d-states, followed by a decline, essentially tracking the core-level dichroism.

The magnetic instability observed above the invar concentration (Fe>65%) is characterized further by a diffuseness in the spectral distribution and an increased lifetime broadening of mainly minority-spin states, indicative of magnetic non-collinear disorder.

Spin-polarized appearance potential spectroscopy of $[\text{Fe}_x\text{Co}_{1-x}]/\text{Cu}(001)$

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We have investigated thin $[\text{Fe}_x\text{Co}_{1-x}]/\text{Cu}(100)$ alloy films with spin-polarized appearance potential spectroscopy (SP-APS). APS is an excellent technique for studying multicomponent systems because it is element specific due to the involved core levels. The short probing depth of electrons makes APS surface sensitive. Since the shape of the spectra gives information about the density of unoccupied states, APS is also sensitive to the structure of surface/film under investigation. With the use of spin-polarized electrons for excitation, APS measures the magnetic properties of the sample by probing the spin-dependent densities of unoccupied states. Our APS study on thin alloy films is complemented by a structure analysis with low-energy electron diffraction (LEED) and magnetic measurements with magneto-optic Kerr effect. Both Fe and Co are known to grow pseudomorphically on fcc Cu(001) for the first 10 atomic layers (AL). While Fe changes its structure from fcc to bcc for thicker layers, Co continues to grow in a fcc structure in a wide range of thickness. Therefore, for the 9-AL alloy films investigated in the present work, a pseudomorphic fcc structure is expected independent of x . However, the Fe-rich films with x between 0.6 and 0.9 exhibit a bcc-like structure as shown in the structure-sensitive APS spectra. This appearance of the equilibrium bulk structure of Fe is presumably induced by the Co „impurities“. The Co spectra, on the other hand, do not show significant changes upon varying x , which points the coexistence of two phases, Fe-rich bcc and Co-rich fcc structure. The magnetic properties were investigated by means of SP-APS and magneto-optic Kerr effect in situ on the same sample. The results of both techniques are in excellent agreement, proving that the spin asymmetry is a good measure of magnetization. The remanence as a function of the composition shows an abrupt change at $x=0.5$ and $x=0.9$. The first might be caused by the structural changes described, which is also reflected in significant changes of the magnetic hysteresis and in LEED. The latter is explained by magnetic reorientation transition from in-plane to out-of-plane easy magnetization, the easy axis in pure 9-AL Fe films on Cu(001). In addition SP-APS allows to detect element-selective contributions to the magnetization. We found the Co magnetic moment in the Fe-rich films to be enhanced similar to the Fe magnetic moment in FeNi₃. [1]

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Band mapping of single crystal molybdenum disulfide*

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All MoS₂ (0002) single crystals investigated in this study were in the form of the natural mineral molybdenite, obtained from Ward's Natural Science establishment. A clean well-ordered surface of MoS₂ (0002) was obtained by cleaving the top layers immediately before transfer into the UHV system followed by a short anneal at 600C. The valence electronic structure of single crystal MoS₂ was measured by synchrotron based, angle-resolved photoemission using an imaging photoelectron spectrometer at beamline 8.0 of the Advanced Light Source. Photoelectron angular distribution images at a fixed kinetic energy were collected for a variety of photon energies. These images represent constant-energy contours in the MoS₂ band structure. A set of such images can be assembled into a complete band structure of MoS₂. The constant energy contours are compared with band maps calculated within the local density approximation (LDA). We observe the valence band maximum (VBM) to be at the Gamma point with the appearance of features at the K-point 0.6 eV below the VBM. Using the experimental geometry that is reported in the literature the LDA calculations show the K-point features to be 1.1 eV below the VBM. Starting with the experimental geometry we have minimized the total energy by allowing the Mo-S bond length to relax, while holding the, a and c lattice parameters at their experimental values. The minimum energy occurs when the S atoms relax outwards with a 1.3\% increase in the bond length relative to the experimental value. The K-point features corresponding to this relaxed geometry are only 0.7 eV below the VBM, in much better agreement with experiment. The experimental bandwidth is 7.9 eV, compared to the value of 7.0 eV obtained in the calculations. The calculations indicate significant band dispersion along the direction perpendicular to the planes.

*The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL. C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD and N. Franco by the Spanish education and culture office.

Spin Polarized Photoemission Study of Magnetite Films: extraction of the bulk polarization via a substrate overlayer model

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Many materials have been predicted to be half metallic magnets, yet, despite extensive study, remarkably little truly compelling evidence for half metallic behavior has emerged. One technique that can potentially yield a definitive answer to the question of half metallic character is spin polarized photoemission and it is from this technique that the most compelling evidence to date has emerged [1]. However such experiments are frequently hampered by the difficulty in producing clean stoichiometric surfaces with a polarisation that is truly representative of that of the bulk material. We have used the spin-resolving photoelectron spectrometer of the Spectromicroscopy Facility (Beamline 7) at the Advanced Light Source [2], to study the half-metallic candidate material magnetite, Fe_3O_4 , which holds out the possibility of use in spintronic devices as a pure spin source. The epitaxial magnetite films were grown at UCD and PNNL by reactive sputtering, or evaporation, onto MgO substrates, with precise control of gas flows and substrate temperature. Their structural and magnetic properties were characterized by RHEED, LEED, XRD, and magneto-transport measurements. We have demonstrated that harsh cleaning of the samples by techniques such as ion bombardment will result in the loss of their spin polarization. However, our ability to perform spin resolved experiments at higher photon energies, (as a direct result of the high brightness of the 3rd generation synchrotron source), has enabled us to study the polarization of the near Fermi edge region of the samples "as received", without having to resort further to such potentially destructive cleaning techniques. By measuring the polarization as a function of emission angle and photon energy, and combining these measurements with a substrate overlayer model, we have been able to extract the underlying polarization of the bulk material and have demonstrated that it is significantly higher than the 30% initially observed in the "as-received" samples, and may indeed be up to 100%. Furthermore, our spin resolved spectra demonstrate close agreement with simulated spectra derived from theoretical one electron density of states calculations [3]. Further experiments are in progress.

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X-ray absorption and soft x-ray fluorescence analysis of KDP optics

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Potassium Dihydrogen Phosphate (KDP) is a non-linear optical material used for laser frequency conversion. Functioning KDP optical components are diamond machined, solvent cleaned, annealed in air (160°C) and then coated with a silica sol-gel. The porous sol-gel coating provides a reservoir of water absorbed from the air and wicks up the dissolved KDP, forming dissolution pits when the KDP crystals are exposed to ambient humidity. However, previous investigations have shown that KDP optics are less susceptible to pitting following annealing, indicating that a modification of surface chemistry has occurred. X-ray absorption and fluorescence were used to characterize changes in the composition and structure of KDP optics as a function of process parameters. KDP native crystals were also analyzed to provide a standard basis for interpretation. Surface sensitive total electron yield and bulk sensitive fluorescence yield from the K 2p, P 2p (L2,3-edge) and O 1s (K-edge) absorption edges were measured at each process step. Soft X-ray fluorescence was also used to observe changes associated with spectral differences noted in the absorption measurements. Results indicate that annealing at 160°C dehydrogenates the surface of KDP resulting in a metaphosphate surface composition with K:P:O = 1:1:3.

NEXAFS Study of tris-(8-Hydroxyquinoline) Aluminum (Alq) and its Derivatives

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The changes in the electronic structure of Alq as a function of methyl and metal substitution are investigated using near-edge x-ray absorption fine structure. In a previous study Curioni et al explained the distinct features of the observed spectra in terms of contributions from different atoms and molecular orbitals. These assignments of the spectral peaks served as a reference for evaluating changes in NEXAFS spectra due to synthetic modification of metal tris-quinolate molecules in our studies. NEXAFS spectra of the C and N edges for a series of vapor deposited thin films of metal tris-quinolates and methyl-substituted tris-quinolates of Al Ga and In will be presented, and the effect of methyl substitution on the electronic structure will be demonstrated.

**DETERMINATION OF THE ADSORPTION SITE BY HIGH RESOLUTION CORE LEVEL
PHOTOELECTRON SPECTROSCOPY OF ADSORBATE AND SUBSTRATE ATOMS**

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High-resolution X-ray photoelectron spectroscopy of core levels using synchrotron radiation is a powerful tool to determine the surface sites of adsorbed atoms and molecules. In particular, the combination of core level photoemission of adsorbate and substrate atoms has proved successful if various different adsorption sites have to be considered. This is illustrated in the present work for the adsorption of CO on a Pd(111) surface. Although the first investigations of this adsorption system date back to more than 25 years, recent experimental and theoretical work [1-3] has shown that the situation is more complicated than originally anticipated. Here we have used the decomposition analysis of the C 1s and Pd 3d core level photoemission spectra, recorded with high resolution at the synchrotron radiation facility MAX II in Lund, to identify characteristic fingerprints of various CO-Pd(111) bonding configurations. It has been found that CO adsorbs in a mixture of fcc and hcp three-fold hollow sites at 0.5 monolayer (ML) in the low temperature (120K) $c(4 \times 2)$ structure, in agreement with the reported literature [2,3]. Near CO saturation coverage (0.75 ML at 120K) additional features appear in the C 1s and Pd 3d spectra due to the occupation of on-top and bridge sites. For CO adsorption at 300K two types of sites are occupied by the CO molecules, as evidenced by the presence of two components in the C 1s and Pd 3d spectra. At coverages up to 0.1 ML only fcc three-fold hollow sites in a local $(\sqrt{3} \times \sqrt{3})R30$ structure are occupied. The population of these sites continues with increasing CO coverage up to 0.32 ML, but in addition CO adsorption in bridge sites occurs. The latter sites are considered to form domain boundaries in the $(\sqrt{3} \times \sqrt{3})R30$ phase. Between 0.32 and 0.5 ML, the maximum CO coverage at 300K, the CO adlayer contains three-fold hollow and bridge adsorption sites, the latter in the domain boundary regions, which introduce poor long-range ordering as observed in LEED. The core level photoemission results are supplemented by high-resolution electron energy loss spectroscopy results, in which the two CO adsorption phases at 300K are clearly distinguished by two C-O stretching frequency components.

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Supported by the Austrian Science Foundation and the EU-TMR Programme ERB FMGE CT98 0124

Non-Dipole Effects in Molecular Photoemission

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Over the past two decades, the dipole approximation has facilitated a basic understanding of the photoionization process in atoms and molecules. Our experiments on the 1s inner shells of small molecules at relatively low photon energies (less than 1000 eV) show strong non-dipole effects. They are significant and measurable at energies close to threshold, in conflict with a common assumption that the dipole approximation is valid for photon energies below 1 keV.

The effect is attributed on basis of concomitant theoretical analysis to the displacement of the 1s charge distributions from the molecular center of mass, providing a much larger effective charge distribution of molecular dimensions consequent of rotational averaging over which the phase of the incident radiation can vary significantly [1].

The experiments were performed at the Advanced Light Source on undulator beamline 8.0 during two-bunch mode. Four time-of-flight (TOF) electron analyzers collect spectra simultaneously at different angles. The present results illustrate that many photoemission experiments on gases, solids, and surfaces can be influenced at relatively low photon energies, pointing to a general need for caution in interpreting angle-resolved photoemission data.

The authors thank the staff of the ALS and the IBM, LBNL, LLNL, the University of Tennessee, and Tulane University collaboration for their support. This research is funded by the NSF (PHY-9303915), the DOE EPSCOR, Research Corporation, and The Petroleum Research Fund. The ALS is supported by the DOE under Contract No. DE-AC03-76SF00098.

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Strong Electron Correlations in Strictly One-Dimensional Chains of Surface Atoms

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The class of (3×1) reconstructions on the Si(111) surface induces linear chains of both adatom and silicon surface atoms. While alkali atoms are known to form a semiconducting surface, the additional electron brought in by an alkaline-earth adatom would then, in a non-interacting electron picture, be expected to form a band metal. Photoemission experiments carried out on the Ba (3×1) system in fact lead to the confirmation of four surface bands ascribed to silicon in the now widely accepted honeycomb chain-channel model of the reconstruction. However, contrary to expectation, the system is found to be insulating, with a gap below the Fermi level of ~ 0.5 eV. Since no additional band is detected that could be related to an incompletely ionized adatom, the system is identified as a one-dimensional (1D) Mott-Hubbard insulator at half-filling.

The electronic bandstructure data taken across various Brillouin zones at low temperature reveal as key features i) the complete absence of dispersion of the lower Hubbard band orthogonal to the chain direction, thus identifying it as virtually perfectly one-dimensional, and ii) a sideband splitting off above the lower Hubbard band near the center of the Brillouin zone. This low energy excitation has a weaker dispersion than the main band and is eventually separated by ~ 0.3 eV. Combined with its decreasing weight, those two bands have the characteristic signature of spin-charge separation in the spectral function of a correlated insulator. The phenomenon is discussed in the framework of 1D t-J models.

Mirroring doubly excited resonances in argon*

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The combination of high photon resolution and differential photoelectron spectroscopic techniques has allowed the discovery of new spectral features in the low-energy photoionization spectrum of argon.

Previously, the high resolution total cross section measurements[1,2] were thought to show all the resonant (singly excited) structures present in the region up to the 3s ionization threshold. However, we have now observed two new weak and narrow LS-forbidden doubly excited resonances in the $3p^{-1}_{1/2,3/2}$ partial cross sections.

They exhibit «mirroring» profiles (opposite lineshapes) which make them undetectable in the total cross section due to essentially total cancellation.

The experiment was performed at the Advanced Light Source on the high intensity and high resolution Atomic and Molecular undulator beamline 10.0.1. A photon bandwidth of 3 meV, necessary to carry out the measurements, was used. The photoelectron spectra were recorded with two complementary experimental setups: a hemispherical analyzer fitted with an Integrated Sensors Ltd (ISL) position sensitive detector and a system of two time-of-flight electron energy analyzers.

The mirroring character of the resonances can be qualitatively understood within a theoretical framework recently developed by Liu and Starace [3]. However, no accurate calculations are available yet for the current example. These new results [4] demonstrate that highly differential studies are necessary to observe certain types of spectral features which also provide additional guides and stringent tests for the inclusion of electron correlations and relativistic effects in atomic calculations.

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* Work supported by the Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences Division.

Adsorption of O₂ on Polycrystalline Re Metal at Room Temperature Studied by Synchrotron X-ray Photoemission Spectroscopy*

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The oxidation and reduction reactions of Re are of importance because Re is a frequently used catalyst material. Furthermore, it is also of environmental interest because the redox properties of Re are similar to those of Tc, which is a critical contaminant in nuclear wastes. In our experiments designed to understand the redox of Re, a clean polycrystalline Re surface is exposed to O₂ in vacuum, and its oxidation is monitored using synchrotron X-ray photoemission spectroscopy.

Clean Re surfaces were made by sputtering and annealing in UHV. The clean surfaces were then exposed to O₂ in the pressure range of 10⁻⁸ to 5 torr at room temperature. Core level spectra of the Re 4f and O 1s were acquired at photon energies of 200 and 800 eV, respectively, from clean and O₂ exposed surfaces. The intensity of the O 1s peak increases, and its position shifts to lower binding energy (by as much as 0.5 eV) as O₂ exposure increases. New features appear in the Re 4f spectra after the clean surfaces were exposed to O₂, and they are higher in binding energy than the original metallic feature. At lower exposures, a new feature (P1) with a higher binding energy appears approximately 0.4 eV away from the metallic feature. At higher exposures, at least one more new feature (P2) appears further (more than 0.8 eV) away from the metallic feature.

The most O₂ exposed surface was annealed at various temperatures (for 5 minutes at each temperature), and spectra of the Re 4f and O 1s were acquired after each anneal. For annealing temperatures up to 300°C, the intensity of O 1s peak does not change, but its position shifts progressively to higher binding energy with increasing temperature. While the overall intensity of the new Re 4f features remains the same as the temperature is elevated to 300°C, the intensity of P2 increases relative to P1. At higher annealing temperatures, the intensity of the O 1s peak decreases, as does the intensity of P2 relative to P1 in the Re 4f spectra. The O 1s peak cannot be completely eliminated by annealing, even at 1000°C.

While equilibrium thermodynamic calculations predict that Re₂O₇ is the most stable phase in the O₂ pressure range used in the exposure experiments, the Re 4f results from these experiments indicate that the most oxidized state of surface Re atoms is less than 4+. The increase of O₂ uptake with O₂ pressure and exposure suggests that the adsorption of O₂ on Re metal is controlled by kinetics rather than thermodynamics. A model is developed to interpret the results from both exposure and annealing experiments.

Electronic Structure of MoS₂ clusters using X-ray Absorption and Emission Spectroscopes

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Molybdenum disulfide (MoS₂) nanoclusters have demonstrated to be effective photocatalysts for the detoxification of chemical waste. In such an application the cluster would absorb light creating electron-hole pairs and thus catalyze specific chemical reactions. For these applications the cluster must have a band gap that is matched to the visible spectrum and the valence and conduction band edges must be compatible with the redox potentials for the reactions involved. To tailor these properties for a specific application we measure the valence and conduction band edges of well-defined MoS₂ clusters using x-ray absorption and emission spectroscopes. MoS₂ clusters from 1-10nm in diameter were formed using the inverse micelle synthetic process at room temperature in inert oil. The cluster size and distribution could be precisely controlled using a high-pressure liquid chromatography system. By measuring the S 2p absorption we are able to measure the change in the conduction band edge of the MoS₂ clusters as a function of particle size. We found that the conduction band edge was blue shifted with decreasing cluster size with shifts up to 1.2 eV measured for clusters 2nm in diameter. These results agree with earlier predictions of the conduction band shifts as a function of particle size. The valence band density of states was determined by measuring the soft x-ray emission from the S 2p core hole. A shift in the valence band edge together with a dramatic change in the density of states was observed with decreasing cluster size. For 2nm clusters a valence band shift of approximately 1.0 eV was measured. This does not agree with effective mass calculations, which predict little or no shift in the valence band edge. We compare these results to recent optical measurements. This work is supported by US Department of Energy under contract number DE-AC04-AL8500 and W-7405-ENG-48.

Reaction mechanism and adsorbed states of cyclohexene on Si(100)(2x1)

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The interaction between the π bond of ethylene and the Si dimer of Si(100)(2x1) leads to the formation of SiC di-sigma bond [1]. This reaction may look like a kind of [2+2] addition reaction, but such [2+2] reaction is thermally forbidden. Here, the asymmetric dimer should play an important role for the reaction: the up atom of the dimer (UD) acts as Lewis base and the down atom at the same dimer (DD) acts as Lewis acid. Thus, in this reaction, ethylene is nucleophile and the DD of the dimer is electrophile. Therefore, we think that the di-sigma bond formation consists of two steps: firstly the DD is attacked by the π bond of ethylene to form a carbocation-like intermediate, and the UD gives a pair of electrons to the positively charged carbon atom in the intermediate, resulting in the formation of the di-sigma bond between the molecule and the Si dimer. This proposed mechanism can explain a recent experimental result which has reported that the adsorption of ethylene on Si(100)(2x1) is stereo-selective [2]. Based on this mechanism we can predict adsorbed states of unsaturated cyclohydrocarbon molecules on Si(100)(2x1), where the di-sigma bond formation reaction is limited to a π -cis addition σ reaction.

In this study, adsorption states of cyclohexene on Si(100)(2x1) have been investigated by means of photoelectron spectroscopy (PES) and scanning tunneling microscopy (STM) as well as the first principle calculations. Cyclohexene may take two conformations in a free molecule, but at room temperature a half-chair conformation is predominant. On the Si(100)(2x1) surface two adsorption states are observed by STM. One shows a rather symmetric bright image and the other is asymmetric with some protrusions. We assign the symmetric one to the di-sigma bonded adsorption state with a boat-conformation, and the other to that with a chair conformation, respectively. These two adsorbed states coexist at room temperature and each state is stable. Hot precursor states may play an important role for reaction products (= adsorbed structures). If the conversion between two states is deliberately controlled, it could be used as a single molecular memory.

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Metastable Atom Electron Spectroscopy of the outermost surface and the molecule-substrate interface of self-assembled monolayer on Au(111)

Metastable Atom Electron Spectroscopy of the outermost surface and the molecule-substrate interface of self-assembled monolayer on Au(111)

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Self-assembled monolayers (SAMs) have gained increasing interest because of their functions and excellent models for examining the principle of molecular self-assembly (SA) mechanisms on metal surfaces. We can give various functions to SAMs by introducing functional groups into the molecules. It is important to investigate the outermost surface of the SAMs and the molecule-substrate interface, since the functional group at the outermost surface controls surface properties of the SAMs, and the interface plays an important role in the SA mechanism. However, the existence of large functional groups will cause the lattice mismatching between molecules and the substrate.

In this study, metastable atom electron spectroscopy (MAES) and ultraviolet photoelectron spectroscopy (UPS) were used to characterize the molecular orientation and the valence band structure of the 8-bromo-1-octanethiol (8BRT) SAMs and 1-octanethiol (OT) SAMs, which were grown on Au(111) substrates with ethanolic solution. We also studied structures of them by a scanning tunneling microscope. Temperature dependencies of MAES and UPS were measured to study the difference of desorption mechanisms of both SAMs. The results of MAES and UPS of 8BRT SAMs indicated that (i) the molecules are oriented with their alkyl chain nearly normal to the Au(111) surface, and (ii) the Br atoms exist at the outermost surface of the SAMs. These results are consistent with those for 8BRT SAMs prepared with hexanolic solution [1]. The temperature dependencies of MAES and UPS of the 8BRT SAMs showed that (i) the molecules are mainly physisorbed on the Au substrate, and a small number of the molecules are chemisorbed, and (ii) the physisorbed molecules desorbed at about 323 K. After evaporating the physisorbed molecules by the heat treatment of the 8BRT SAMs, the electronic states due to the chemical bonding between the S atom of 8BRT molecule and the Au substrate were firstly observed. The adsorption and desorption mechanisms of the 8BRT SAMs and OT SAMs will be shown at the conference with STM images of these SAMs.

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Resonant Photoexcitation of Si(001), (111) measured with Two-Photon Photoemission.

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Two-Photon Photoemission (2PPE) of Si(001) and (111) surfaces are measured to elucidate photoexcitation processes. The experiment was performed with a 100 fs laser light in the wavelength region between 270 and 335 nm. 2PPE spectra measured with different photon energies revealed several sharp structures. The 2PPE structures shift with one or two times of the photon energy increment allowing determination of the excited intermediate state and the occupied initial state. The intensity of the 2PPE structure showed resonant enhancement. A resonance between an occupied state at $E_F - 0.46$ eV and a normally unoccupied state at $E_F + 3.49$ eV was observed for both (001) and (111) surfaces. The relevant states are assigned to the bulk bands on a basis of polarization dependence and on of a comparison with the known band structure. Two further structures were observed for Si(111) surface. The structures are assigned to be due to the surface states at 0.6 and 1.9 eV above E_F .

All of these 2PPE structures exhibit similar tendencies: a) the width of the 2PPE structure is less than 0.3 eV FWHM, and b) the structure is visible only within limited wavelength region indicating that the resonance width is about 0.3 eV. The sharpness is an advantage over the commonly used UPS and IPES which generally show structures as broad as 1 eV. This work demonstrates the capability of 2PPE which allows simultaneous identification of occupied and normally unoccupied states. It is noted that the excited surface state is visible only within the resonance width with the occupied surface state. Hot electrons in the bulk bands are not very effective to build up population in the excited surface state. The sharpness of the resonance suggests that photon-induced chemical reaction at silicon surface is strongly wavelength dependent. Selectivity of chemical processes may be improved with finely wavelength tuned laser radiation.

Improving The Performance Of The Scanning Transmission X-ray Microscope STXM IV With A Dedicated Integrating Multi-segment Silicon Detector

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We report on progress in the commissioning of the room temperature scanning transmission X-ray microscope "STXM IV", operating at beamline X1A of the NSLS at Brookhaven National Laboratories. NEXAFS information of sub-50nm regions with an energy resolution of 0.1eV - 0.4eV (for 280eV, 800eV photon energy respectively) are obtained routinely in the energy range of 280eV to 800eV, including the K-edges of Carbon, Oxygen and Nitrogen. The microscope operates in a closed Helium atmosphere to eliminate air absorption.

A novel integrating multi-segment Silicon detector is being commissioned which will increase the performance of the X-ray microscope considerably. At very high rate capacity (>10 MHz photon rate) it operates with a very low noise of only 5 photons per pixel per detector element (corresponding to 10 kHz of noise in the absorption contrast mode) without any cooling of the chip or the readout electronics. The segmentation allows the use of additional imaging modes (compared to the absorption contrast with incoherent photon detection) without making changes in the microscope configuration. In dark field contrast, which is a powerful method to visualize small (sub-50nm) immunogold labels in biological applications, x-rays that are scattered out of the illuminating aperture are collected. Using an additional optical element upstream of the focusing optic we can also switch to Nomarski phase contrast mode, which is particularly useful for imaging interfaces between regions that show little absorption contrast, but a significant difference in the real part of the refractive index, like a number of polymer blends.

We would like to acknowledge T. Beetz, M. C. Dayton, J. Kirz (SUNY Stony Brook) for their contribution to the design and commissioning of the STXM IV microscope. The Nomarski phase contrast experiments have been performed in collaboration with D. Joyeux (Institut d'Optique, Orsay, France) and F. Pollack (Centre Universitaire, Orsay, France), who also supplied the necessary optical element (wave front profiler).

Elastic Scattering of Low- and Medium-Energy Electrons on Molecules: Influence of Non-Spherical Potentials in Multiple Scattering Calculations*

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Elastic scattering of 10-1000 eV electrons from free molecules is studied using a novel multiple-scattering approach based upon a curved wave expansion of the electron wave function around each of the atoms of the molecule. Space filling non-spherical potentials derived from quantum chemical calculations on the ground state of the molecules have been employed to represent the atomic scattering centers, resulting in good agreement with available experimental data for the angular distributions of elastically-scattered electrons. The importance of using non-spherical corrections to the atomic potentials is pointed out by comparing with similar results obtained using spherical atomic potentials calculated for isolated atoms. These corrections are small for energies above 100 eV, but they become increasingly significant at lower energies. The role played by the exchange and correlation part of the scattering potentials has also been investigated. These results should also have implications for other electron scattering problems such as those encountered in low-energy photoelectron diffraction from both core and valence levels.

* Work supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. DR, RDM, and FJGA acknowledge help and support from the German Fulbright Commission, the Basque Government, and the Spanish Fulbright Commission (Grant No. FU-98-22726216), respectively.

Subnatural-Width Angle-Resolved Resonant Auger Electron Spectroscopy of Atoms and Molecules on the High Resolution Soft X-Ray Monochromator at SPring-8

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A high-resolution plane grating monochromator installed on the c-branch of the soft X-ray figure-8 undulator beamline 27SU, nicknamed soft X-ray photochemistry beamline, at SPring-8 provides linearly polarized monochromatic soft X-ray at a very high photon energy resolution up to 20,000. One of the unique features of this beamline is that the direction of the polarization vector for the first-order harmonic photon generated by the figure-8 undulator is horizontal whereas that of the 0.5-order harmonic photon is vertical. Thus one can switch the direction of the polarization vector from horizontal to vertical and vice versa by varying a gap of the undulator and thus can perform the angle-resolved electron spectroscopy of atoms and molecules using an electron spectrometer fixed in the horizontal direction.

Recently we have installed a new end-station for high-resolution angle-resolved electron spectroscopy of atoms and molecules. The system consists of an ultra-high resolution SES-2002 hemispherical electron energy analyzer, a GC-50 tunable gas cell, and a differentially pumped chamber (Gamma-Data Scienta). The energy resolution of this analyzer is less than 2 meV at pass energy 2 eV, i.e., at the most stringent setting, and 13 meV at pass energy 20 eV, i.e., at our common settings. To demonstrate the performance on the above described beamline, we present our recent measurement for the resonant Auger electron emission at electron kinetic energy ~ 800 eV in the Ne atom following $1s \rightarrow 3p$ excitation at excitation photon energy 867 eV. In this measurement, the photon band pass is 60 meV, the electron energy resolution is 13 meV, and the Doppler width due to thermal motion of the sample Ne atoms is 80 meV. The overall resolution ~ 100 meV is much smaller than the natural width 250 meV of the Ne $1s$ hole state. Under these conditions we can completely (or partially) resolve the resonant Auger final states $2p^{-2}(^1D_2)3p$ (or $4p$) 2P , 2D , 2F . We present also the measurements for resonant Auger emission in the CO_2 molecule: we demonstrate how vibrational progressions of different modes appear by detuning the excitation photon energy within the broad C, O $1s \rightarrow \pi$ resonances.

Electron Diffraction in Atomic Clusters: a Highly-Convergent Theoretical Approach for Large Cluster Sizes with Application to Photoelectron Diffraction and LEED*

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A new highly-convergent iterative method for the simulation of electron diffraction in atomic clusters (EDAC) is presented. A muffin-tin description of the atomic potentials and an exact representation of the free-electron Green functions are used. The method relies upon a convenient separation of the Green functions involving rotation matrices to reduce the computation time and storage demand. The multiple scattering expansion is iteratively evaluated using a divergence-free variation of the Haydock recursion method, as modified to allow calculating the far-field electron intensity in an arbitrary number of directions from a single multiple scattering calculation. The computational demand scales as $N^2 (l_{\max}+1)^3$, where N is the number of atoms in the cluster and l_{\max} is the maximum of the relevant angular momentum quantum numbers. Example applications to photoelectron diffraction (PD) from Xe adsorbed in Pt(997) and low-energy electron diffraction (LEED) from Si(111)-(7x7) and Gd/W(110) will be discussed. In these calculations, $N > 1000$ is needed for full convergence in the PD results, and $N > 1500$ is required in the LEED results due to the large unit cells involved. The advantages and disadvantages of this approach relative to prior methods (e.g. the Rehr-Albers separable expansion) will also be discussed.

*This work is supported in part by the Director, Office of Science, Basic Energy Sciences, Materials Sciences Division of the U.S. FJGA would like to acknowledge help and support from the Spanish Fulbright Commission (Grant No. FU-98-22726216).

Theory of Multi-Atom Resonant Photoemission*

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Multi-atom resonant photoemission (MARPE) [1] occurs when the photon energy is tuned to a core-level absorption edge of an atom neighboring the atom from which the photoelectron is being emitted, with the emitting level having a lower binding energy than the resonant energy. Significant peak intensity enhancements have by now been observed in various metal oxides, in metallic systems, and in metal halides. A general theoretical description of MARPE which extends prior work will be presented, including a fully quantum mechanical picture of all excitation channels and multiple x-ray scattering. The relationship of this picture to a classical description based upon Maxwell's equations will also be considered. This phenomenon will be compared with the well-known Fano resonances of a discrete level with several continua, and the differences between MARPE and this single-atom case will be discussed.

*This work is supported in part by the Director, Office of Science, Basic Energy Sciences, Materials Sciences Division of the U.S. FJGA would like to acknowledge help and support from the Spanish Fulbright Commission (Grant No. FU-98-22726216).

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Coupling Between Adsorbate Vibrations and an Electronic Surface State

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We report direct angle-resolved photoemission measurements of the coupling between the symmetric stretch vibrational mode of adsorbed hydrogen and a surface band on W(110). This coupling is manifested by the surface band being split into two branches at a binding energy comparable to the vibrational mode energy, as confirmed by observation of a dramatic hydrogen/deuterium isotope effect. The electron-phonon coupling parameter λ is found to be significantly larger than that for bulk W, and to be closely related to the degree of surface localization of the surface state wave function.

Metastable helium atom stimulated desorption of H⁺ ion from H₂O/Na/Ni(110) surface

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H⁺ desorption induced by the impact of metastable helium atom (He*) with a thermal kinetic energy has been observed for the H₂O/Na/Ni(110) coadsorption system. The experiments have been carried out using a pulsed-discharge type He* source, which generates He*, He I photon and fast neutral He atoms. Positive ions desorbed by the primary particles were detected by an angle-resolved electrostatic energy analyzer, and their mass-to-charge ratio was specified based on the analysis of their flight time in the energy analyzer. The H⁺ desorption by He* and Na⁺ desorption by the fast He were observed. The H⁺ desorption yield was found to be nearly constant at the kinetic energy range of 50-250 meV, which reflects that the H⁺ desorption is purely due to an electronic process. The H⁺ desorption by He I photon was not observed, indicating that the H⁺ desorption by He* is not stimulated by electrons ejected by He*. Based on the measured metastable deexcitation spectra, we have concluded that the H⁺ desorption by He* is caused by a hole created on a valence level via the Auger deexcitation of He*. The H⁺ desorption may be understood within the framework of Menzel-Gomer-Readhead model. It is emphasized that ions desorbed by metastable atoms derive only from the outermost surface because they create holes only on the outermost surface.[1]

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Combined, STM, XAS and HREELS Study on the Stabilization of One-Dimensionally Ordered π-Bonded Ethylene on Pd(110)

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The adsorption of ethylene on Pd(110) and H-covered Pd(110) was investigated by scanning tunneling microscopy (STM) and near-edge X-ray absorption fine structure (NEXAFS) experiments. Ethylene molecules occupy on-top sites with their C=C axes substantially aligned along [1-10] on both surfaces. At low coverages, ethylene molecules form a short-range (3x1)-1D ordered structure in thermal equilibrium, whereas they have no distinct ordered structure and are stabilized at on-top sites at temperatures below 170 K. The ordering behavior of ethylene molecules is similarly observed on both clean and H-covered Pd(110) in spite of the difference in local symmetry. On the other hand, at a high coverage (0.5 ML) on a clean surface, ethylene molecules form a c(2x2) structure. The origin of intermolecular interactions between ethylene molecules causing a one-dimensional ordered structure at low coverage is discussed.

K-Shell X-Ray Reflection and Absorption Near Edge Structure in Hexagonal BN

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The specular reflection and scattering of ultrasoft x-rays from a surface of the hexagonal BN crystal cut parallel to the c-axis of the crystal has been investigated in the wide energy region including the both B K- and N K - absorption edges using s-polarized radiation. Two orientations of the surface with respect to the electric field vector (E parallel c and E perpendicular c) were investigated. The strong anisotropy of reflection and scattering near absorption edges has been discovered. B K- and N K-absorption spectra for both orientations of the crystal were calculated from the reflection spectra by means of Kramers-Kronig relations and were combined in a unit energy scale by means of XPS-data. A strong orientation dependence of calculated absorption spectra has been showed. The essence of this dependence consists in the different extent of a manifestation of the $1s \rightarrow \pi^*$ ($2p_z \rightarrow \pi^*$ - component) and $1s \rightarrow \sigma^*$ ($e'(2p_{xy})$ - component) transitions depending on the orientation of the crystal. The analysis of the orientation dependence of the calculated absorption spectra shows a possibility to trace the function of the each channel of the excitation in the formation of the fine structure. The investigation of the angular spectral absorption dependencies have demonstrated the different dynamics in creation of the B K- and N K- excitations in BN_{hex}. This conclusion accords well with calculations carried in [1]. According to [1] the B K-excitations are essentially localized within the nearest neighbours and can be assigned to transitions into the atom-like π^* and the localized two-centre σ^* MOs. The π^* interaction within a basal plane as well as between the neighbouring layers can be neglected. The N K- excitations are more delocalized and the essential π^* interaction within a basal plane in this case. The analysis of the orientation dependence of reflection and calculated absorption spectra shows a high sensitivity of the fine structure to vibronic interaction connected with Jahn-Teller distortions and to the local atomic rearrangement.

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New Insights on the Shape Resonances in the K-shell Continua of N₂ and CO Prototype Molecules

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A considerable body of experimental and theoretical works on the soft x-ray photoabsorption for core levels of small molecules has shown that resonance and multielectron effects are commonly encountered. Within the first tens of eV above the core-level ionization thresholds, broad resonances are characteristically found in the photoabsorption spectra of the molecules, and commonly referred as shape resonances because the resonances are interpreted as the temporary trapping of the outgoing photoelectron by a centrifugal molecular potential barrier. Based on the MS calculations, Dehmer and Dill [1] concluded that the shape resonance of N₂ was caused by a centrifugal barrier acting on the *f*-partial wave in the continuum. Analogous interpretation of the shape resonances of CO and NO was suggested by them. And the qualitative explanation of the shape resonances has been widely accepted until our pioneering work [2] on the photoelectron angular distributions from fixed-in-space N₂.

Recently we have re-examined the shape resonances of N₂ and CO experimentally and theoretically at the deep level of the photoelectron angular distributions from fixed-in-space molecules, from which one can extract the dipole matrix elements and phase shift differences describing the photoionization processes. On N₂, we obtained the remarkable result [3], *i.e.*, the shape resonance enhancement appears not only in σ_u channel but also in σ_g channel by the intershell interaction between $1\sigma_g$ and $1\sigma_u$ molecular orbitals, in contrast to the results of MS and HF calculations. On CO, we determined the matrix elements and phase shift differences over the shape resonances in the C- and O-K shell ionization continuum [4-6]. It reveals that the shape resonance above the C-K edge consists of *p*-, *d*-, and *f*-partial waves and the resonance above the O-K edge consists of *s*-, *p*-, *d*-, and *f*-partial waves, in contrast to the widely accepted explanation of the single *f*-partial wave enhancement.

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Observation of Post-Collision Interaction in Atomic Inner-Shell Photoionization Accompanied by Emission of Two Auger Electrons

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We report the first experimental observation of post-collision interaction (PCI) in inner-shell photoionization accompanied by a two-electron Auger decay process obtained using an electron-electron coincidence technique. In this experimental study,

$\text{Xe}^+ 4d^{-1}_{3/2}$ was formed by monochromatized synchrotron radiation which decays by the emission of two electrons to the $(5p)^{-3,4}\text{S}$ state. We observed the influence of PCI on the lineshape of fast Auger electron in coincidence with second Auger electron of zero-kinetic energy at photon energies close to the $4d^{-1}_{3/2}$ threshold. It was found that the fast Auger peak shifts towards higher energy, and the width of the peak increases, when the photon energy approaches the $4d^{-1}_{3/2}$ threshold. Furthermore, the peak shows a clear asymmetry profile with a tail towards higher energy at the photon energy very close to the threshold. Two different mechanisms can contribute to the decay process namely; the simultaneous ejection of two electrons (double Auger process) or the sequential emission of two electrons (cascade Auger process). Both processes are strongly influenced by PCI[1]. Comparison of the data with theory is in progress to establish which of processes is present.

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Relativistic dirac-fock multi-configuration calculations of energy levels $n=16$ and $n=10,9$ states for O^{4+} with Li-like core*

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We have performed completely relativistic dirac-fock multiconfiguration calculations for high rydberg states $n_1=16$; $l_1=10,9,8,7,6$ and $n_2=10,9$; $l_2 = 9,8,7,6,5$ for O^{4+} ion having a Li-like core $1s^2 2s^1$. The aim of this theoretical investigation is to study the effect of polarizability of the Li-like core for large l_2 values ($l_2 = 8,7,6$) and the contribution to the transition energies of the configuration mixing of doubly ionized states $1s_2 2p\ nl$ for medium l values ($l_2 = 5$). These transition energies for O^{4+} of $1s^2 2s^1\ n_1(n_1 = 16)$ to $1s^2 2s^1\ n_2$ ($n_2 = 10,9$) for l values of 9 to 5 have been measured by laser induced recombination spectroscopy to a very high accuracy of 2×10^{-5} eV [1]. The challenge is to achieve an accuracy in theoretical calculations that would allow us to compare the theoretical values with the very accurate experimental values obtained in [1]. We shall present our effort to make these calculations with relativistic dirac-fock multiconfiguration method.

* Work supported by Alexander von Humboldt Foundation

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Photoelectron Angular Distributions from C and O K-Shells of Oriented CO Molecules; A Critical Comparison between Theory and Experiment

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We have recently measured the angular distributions (AD) of K-shell photoelectrons of oriented molecules in order to elucidate the nature of the shape resonances, the enhancement of absorption cross section occurred usually at several eV above the K-shell ionization thresholds. We report here the study on CO, a typical hetero-diatomic molecules. We have measured the AD of C-1s and O-1s photoelectrons from fixed-in-space CO molecules in their ionization threshold region by the angle resolved photoelectron-photoion coincidence technique. From the experimental angular distributions, we have determined 18 dynamical parameters (10 dipole matrix elements and 8 phase shift differences) for O K-shell, and 16 parameters (9 dipole matrix elements and 7 phase shifts differences) for C K-shell, and compared them with the results of our calculations in the Relaxed Core Hartree-Fock (RCHF) approximation. The theoretical results are in qualitative agreement with the experimental ones. The analysis shows that the sigma-asterisk shape resonance is formed not by the f-wave alone, as it was widely believed earlier, but by approximately equal contributions of three partial waves ($l=1,2,3$) for C K-shell and four partial waves ($l=0,1,2,3$) for O K-shell, with a rather substantial contribution of all other partial waves with l smaller than 5. Furthermore, it is found that several Cooper minima are likely to exist in partial photoionization cross sections, in particular, in the C 1s-sigma \rightarrow epsilon-d-sigma transitions.

Orientation of Surface Molecules Reflected in a Penning Ionization Electron Spectrum. Analysis Based on Local Electron Density Oozing from the Outermost Surface

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The relative intensity of a certain band in a gas-phase Penning ionization electron spectrum (PIES) depends on the "average" distribution of the corresponding molecular orbital (MO) while that in a solid-phase PIES on the local distribution at the externally exposed portion of the molecular surface in the top layer [1]. Theoretical PIES have been synthesized for isolated molecules on the basis of the exterior electron density model [2], which makes the intensity of each constituent band proportional to the probability density of the MO integrated outside the molecular surface. However, the PIES of molecular solids have been analyzed qualitatively by considering anisotropic MO shapes [1]. We synthesize here the PIES of organic films for assumed molecular orientation or arrangement. We confine the integration to a region exposed outside the top layer to calculate local electron density oozing from the outermost surface (LEDOS). Observed and synthesized PIES for ultrathin films composed of the same kind of molecules but prepared under different conditions are compared and the validity of the assumed aggregations is examined. Singular hollows due to the 9pi and 7pi MO in the PIES of a pentacene monolayer on graphite can be reproduced by the LEDOS analysis with flat-on molecular orientation. In contrast, the surface of a 60-layered film is found to have considerably random orientation. It is also shown that marked intensity distribution in the PIES of a pentacene film prepared on a metal substrate is consistent with the LEDOS for orientated crystallites.

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Examination of Band Bending at Sexiphenyl/metal Interfaces Studied by UPS, MAES, and XPS: Charging Effect Induced by Metal Atoms Deposited onto an Organic Thin Film

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Recently, organic semiconductors have attracted much attention in relation to application to organic electronic devices such as organic solar cells, and organic electroluminescent devices. In spite of the extensive studies of fabrication of organic devices, energy level alignment and band bending features of organic-semiconductor/metal interfaces are not yet well understood.

At inorganic-semiconductor/metal interfaces, band bending features have been extensively studied by photoemission technique. When a small amount of metal atoms are deposited on a semiconductor surface, the energy shift of the electronic levels of the semiconductor has been often observed and interpreted in relation to band bending.

In the present study, we have examined band bending at sexiphenyl (6P)/metal (Au, Mg) interfaces using UV photoemission spectroscopy (UPS), metastable atom electron spectroscopy (MAES), and X-ray photoemission spectroscopy (XPS). In the case of the experiment of 6P film deposited on the metal substrate, the energy position of the occupied levels of 6P and the vacuum level were almost constant irrespective of the film thickness upto 20 nm, except the initial abrupt lowering of the vacuum level during monolayer-formation. This result indicates flat band behavior of 6P film in this thickness region. On the other hand, in the reverse case, that is, when Mg atoms were deposited on 6P film, the downward shift of energy levels of 6P was observed. This energy shift is in contrast to the flat band feature observed at 6P on Mg system.

At Au on 6P system, no energy shift was observed with very small amount of photon flux (the sample current was typically less than 2pA). With increasing the photon flux, the energy positions of the peaks in the spectra exhibited energy-shift to higher binding energy side. This energy shift can be ascribed to charging of Au island cluster formed on 6P film. These results demonstrate that we have to clarify what is really observed for metal on organic system by photoemission before discussing the band bending.

Auger Photoelectron Coincidence Spectroscopy from Solids

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Auger Photoelectron Coincidence Spectroscopy (APECS) is a technique in which two electron analysers are used to examine the electron spectra from the surface of solids illuminated by mono-energetic X-rays. One analyser has a fixed energy, while the other scans a correlated feature in the same spectra. As the equipment responds only to electrons that arrive in time coincidence, the experiment is able to measure correlated emission events the same atom. In this way it is possible to build up a better understanding of the processes determining the shape of the spectra. We have applied APECS to the study of Auger lines in the spectra of both 3d and 4d transition elements [1]. Recent advances in the performance of APECS systems have led to a range of new applications of the technique.

We have recently completed high-resolution determinations of the APECS spectra of the $2p_{3/2}$ line in Cu in coincidence with terms in the L_3VV spectra of Cu. We have been able to show that the photoelectron line moves by 300 meV towards higher binding energies in coincidence with the 3F term of the L_3VV compared to its position in coincidence with the 1G term. We believe that this is a consequence of the differences in screening between the two final state configurations. The 3F term is better screened, and so the interaction between the escaping photoelectron and the remaining positive ion is reduced. This dynamic effect changes the position of the photoelectron line and therefore changes the value of the final state hole-hole interaction energy.

We have also been able to show that it is possible to measure the Auger spectra of atoms buried beneath an oxide overlayer by tuning the fixed photoelectron detector to the energy of the clean XPS line while scanning the Auger signal. In this way, the Auger analyser will detect only those atoms that do not have a chemical bond with oxygen. We believe this is a novel and useful technique for studying buried atoms.

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Temperature dependent Ce $3d$ - $4f$ resonant photoemission study of CeFe₂

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CeFe₂ crystallizes in the cubic Laves phase(C15) structure and orders ferromagnetically below TC_230 K. In order to investigate the interactions between the localized Ce $4f$ electron and itinerant $3d$ electrons of Fe in CeFe₂, we have performed the temperature dependent bulk sensitive $3d \rightarrow 4f$ resonant photoemission spectroscopy and x-ray absorption spectroscopy using photon energies corresponding to the Ce $M_{4,5}$ absorption edge with high resolution (~ 100 meV). We observed that the intensity ratio of peak near E_F to that of f^0 final state related peak about 2 eV increases rather abruptly as the temperature is raised above the ferromagnetic transition temperature TC_230 K. Temperature dependent x-ray absorption spectroscopy shows that the value of n_f does not change much with temperature, which indicates that the hybridization strength between $4f$ electron and valence band is almost the same. Therefore, the intensity increase of peak at E_F compared with f^0 related peak about 2 eV in the paramagnetic phase is ascribed to the fact that the density of states at E_F of paramagnetic Fe $3d$ is larger than that of ferromagnetic phase, which was actually observed in the off-resonance spectra. Gunnarsson-Schönhammer calculation based on Anderson single impurity model with using off-resonance spectrum for realistic hybridization $V^2(_)$ well describes the Ce $3d \rightarrow 4f$ resonant photoemission spectra.

Probing Chemical States and Charge Transfer on Modified Sulphide Surfaces: Information from X-ray and Electron Spectroscopies

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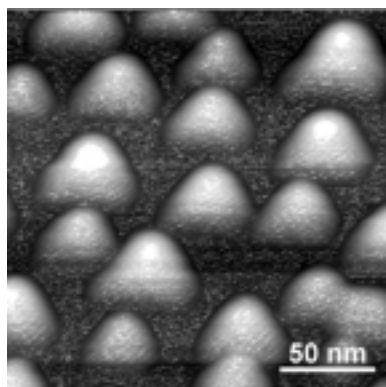
The understanding of reactions on sulphide surfaces has progressed considerably basing on numerous surface analytical and electrochemical investigations. Mechanisms of electronic charge transfer, however, and connections between the reactivity of metal and sulphide centres and surface band structure properties are not yet fully understood.

The first section of the paper reports on surface modification of sulphide minerals (FeAsS and FeS₂) by oxidation on air. The spectra of the pristine surfaces provide evidence of different surface states of all three elements with filled and unfilled dangling bonds, caused by rupture of the Fe-As, As-S and Fe-S bonds. Differently coordinated sulphur surface sites with filled dangling bonds give rise to composite signals in the S2p spectra.

Reaction of oxygen with FeAsS surfaces in UHV reveals fast oxidation of the surface sites giving As(0), As(II), As(III), and As(V) indicating a consecutive reaction scheme involving elementary one-electron transfer steps. The oxidation on air gives As(V) as a final oxidation product. Sulphur oxidation leads to numerous intermediate species with the sulphate being the final product. A model of homogeneous oxidized layers on the minerals indicates that reaction with air has produced a FeOOH layer on top of a increasingly oxidized arsenic and iron containing layer.

In the second section results on the oxidation of the organic adsorbate from 2-mercaptobenzothiazole (Hmbt) on the CdS(1010) are presented. Photon induced electron-hole pair generation influences the oxidation of the Cd-mbt adsorbate at the solid/electrolyte interface causing a strong increase of the electron transfer rate across the surface illuminating the sample by daylight.

The thermally activated chemisorption of Hmbt in the chemisorption/oxidation/dimerization sequence becomes rate-controlling during daylight exposition increasing the coverage rate by the oxidation product.



Multilayer Relaxation of Al(100) and Al(110) Surface: An ab initio Pseudopotential Study

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The multilayer relaxations of Al(100) and Al(110) surface are studied using the plane wave ab initio pseudopotential method within the local density functional theory. Our calculations show that the surface relaxation of Al(100) is an "anomalous" outward relaxation (1.89%), and is in excellent agreement with published experimental results (1.8%). This is in contrast to several previous empirical and semi-empirical theoretical studies whose predictions are in contradiction with experiments. For the Al(110) surface, our results show inward relaxation, which is consistent with experiments (LEED) and other theoretical calculations. The origin of "inward" and "outward" relaxation is discussed. The surface energy and surface electronic properties are also studied in this work.

Comparison of MEED- and XPD-diffraction patterns on Cu(001)

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Increasing the electron energy in a LEED-experiment changes the diffraction pattern from the usual LEED-pattern, which reflects the reciprocal surface lattice, to a pattern similar to the XPD-experiment, from which information on the real crystal lattice can be derived. The high signal to noise ratio in the MEED-experiment allows very fast data aquisition compared to the XPD-experiment.

Recently, a model has been proposed by Vicente et al., which describes the LEED-MEED-transition and the MEED diffraction pattern. The two main ingredients of the model are the excitation/absorption of phonons during electron scattering, which leads to a smearing out of the sharp LEED-peaks, and the multiple scattering of the electrons, which is responsible for the XPD-like diffraction pattern at medium energies.

Measurements of the angular distribution of electrons backscattered from Cu(001) show characteristic differences between the MEED- and XPD-patterns. The MEED-measurements were performed with a moveable electron gun, which permitted the use of different scattering angles. At an arbitrarily chosen scattering angle of 56 degrees, the MEED- and XPD-patterns are mostly similar. However, a symmetry in the MEED-polar intensity plots (PIPs) is observed with respect to the half scattering angle, and additional peaks are to be seen. Theoretical analysis with the Vicente-theory show that peaks in the MEED-PIPs are due to forward focusing in either the incoming or the outgoing part of the electron trajectory, or they are due to interferences between waves with foward scattering in the both the incoming and the outgoing direction [1].

The choice of a scattering angle equal or near an angle between low-index crystal axes leads to very drastic differences in the MEED- and XPD-patterns. Measurements at scattering angles of 72 degrees (the angle between facing [112]-axes) and 90 degrees (angle between facing [101] axes) were performed at different energies. Under these conditions, the 00- and higher indexed LEED-peaks can persist up to energies exceeding 1KeV, in contrast to the measurements at arbitrarily chosen scattering angle, where they exist only at energies below 400 eV. As these peaks are caused by elastic scattering processes with no or little phonon excitation/absorption, those processes are still important at medium energies under these conditions.

These results suggest that great care must be taken considering the interpretation of a MEED-experiment, as under the circumstances described above, very important differences in the XPD- and MEED-diffraction patterns exist.

Study On Electronic Properties And Bonding Configuration At BN/SiC Interface

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The electronic properties and bonding configuration at the interface between cubic (zinc blende) BN and 3C-SiC are studied using the first principle linear muffin-tin orbital (LMTO) method based on local-density-functional (LDA) theory. The (001) superlattice of BN(n)/SiC(n) (n=1-5) is used to study the interface. The calculated results show that the preferred bonding configuration is Si-N and C-B for the (001) BN/SiC interface. The formation energy of the interface is studied as a function of thickness of the superlattice. The origin of the bond formation as well as the electronic properties of the interface are also investigated.

Effect of Gamma Irradiation on the Electronic Structure of Bi-2223 Superconductor

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An XPS investigation was carried out on Bi-2223 superconductor, in an effort to study the effect of gamma-irradiation. There is no change in the binding energies of Bi 4f, Ca 2p, Cu 3d, O 1s, Pb 4f, and Sr 3p core levels up to gamma dose of 50 Mrad. However, for the gamma dose of 60 Mrad, Bi 4f region shows two sets of spin-orbit split levels, one set being at the same values as that of the low-dose samples and the other set at about 3 eV higher binding energy. Also for this high-dose sample, (i) O 1s region clearly shows the removal of O by gamma irradiation, (ii) Cu 3d_{3/2} region shows no satellite, which is typical of Cu 2+ valence state, and a low energy shoulder that is a signature of Cu 1+ valence state, in contrast to the low-dose samples. These observations seem to suggest a reduction of hole concentration in the Cu-O planes through O removal at a gamma dose between 50 and 60 Mrad.

The Role of the Second-order Processes in the Formation of Extended Fine Structures of Auger Electron Spectra and their use for Analysis of the local Atomic Structure of Hyperfine Surface Layers

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Extended fine structures (EFS) in 3d- and 4d-metal secondary electron (SE) spectra were revealed more than 25 years ago. SE spectra EFS consists in oscillations of the emission intensity (the period is ten eV and the extension is hundred eV) which are located on the high-energy side from the CVV Auger-line. EFS were demonstrated to form as a result of the coherent scattering of SE on the local atomic surroundings of an ionized atom, i.e. they are the EXAFS-like phenomena. But contrary to the rest EXAFS-like phenomena, the nature of the SE spectra EFS formation appears to be far more complex. Namely, this EFS is formed both in processes of the direct emission of the secondary electron from an atom to the finite state and as a result of the second-order process connected with the generation and the further relaxation of the intermediate state. The latter process is analogous to the automation process (of the Fano effect), however in the case of the process which forms the SE spectrum EFS in the second-order process the intermediate state is characterized by a hole on the inner level and an electron in the continuous spectrum as opposed to the classic autoemission process where the electron in the intermediate state is in a certain resonance state. By virtue of the presence of the first- and second-order processes the SE spectrum EFS is determined by processes of the coherent scattering of both an electron of the finite state and an electron of the intermediate state; i.e. in the nomenclature of EXAFS the SE spectrum EFS is determined by oscillations of two types which depend on interatomic distances and different wave numbers. Taking account of two types of oscillations makes possible to describe adequately main characteristic features of the SE spectra EFS which set off it from all the rest EXAFS-like phenomena. Apart from the fact that the SE spectra EFS is an effect of non-resonance processes of the second order in the formation of Auger electron spectra, these structures can be used for determining parameters of the local atomic environment in hyper-fine surface layers of a matter under study. To determine parameters of the local atomic structure, i.e. the atomic pair correlation function (PCF), from experimental SE spectra EFS, the Tikhonov method of solving inverse ill-posed problems which was developed for EXAFS is used. The use of this method makes possible, within the context of the solution of the inverse problem, to take account of oscillations of two types which form SE spectra EFS. Within the framework of this formalism atomic PCF and parameters of the nearest atomic environment have been obtained from the Fe, Ni, Cu experimental EFS MVV spectra. As a result an insignificant decrease of the nearest interatomic distance and marked right-handed asymmetry of peaks of the atomic PCF by the analysed layer depth (~ 5 Å). Obtained interatomic distances are in good agreement with the LEED results and results on the asymmetry of PCF peaks can be correlated with both the presence of the anharmonicity of surface atom fluctuations and effects of averaging of calculated PCF over the analyzed layer depth.

Financial support was provided by the RFBR grant No. 00-03-33049

Ultrahigh-resolution photoemission spectroscopy of simple metals : Direct observation of superconducting gap and phonon-induced fine structures

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Photoemission spectroscopy has played important roles to study the electronic structures near the Fermi level (E_F) of high temperature superconductors (High- T_c) because of the drastic increase of the energy resolution during the last decade. This success could be ascribed to the comparable energy scales of the structures to the resolution of spectrometers. For researching electronic structures having smaller energy scales, such as the superconducting gap of low- T_c superconductors, we have been constructing a low-temperature (>4 K) ultrahigh-resolution (1.4 meV) photoemission spectrometer.

In this study, we will present first photoemission result of the superconducting gap of simple metals. We have measured niobium ($T_c=9.26$ K) and lead ($T_c=7.19$ K) at temperatures below and above T_c . Below T_c , we observed a shift of leading edge and an appearance of a sharp quasiparticle peak just below E_F (~ 2.5 meV) in each sample, both of which are characteristic of superconducting-gap opening. In addition, we found several fine structures in the region higher than the quasiparticle peak position in the lead spectrum, which are not so obvious in the niobium spectrum. From a comparison between the present result and a tunneling result [1], we attribute them to phonon-induced ones. The difference in the superconducting spectral shape reflects a difference of the strength of electron-phonon coupling ($2D/k_B T_c = 3.8$:Nb 4.3 :Pb [2]). From a temperature-dependent study of niobium across T_c , we found the gap size obeys theoretical predictions [3]. These results demonstrate the potential of photoemission spectroscopy for investigating of electronic structures with smaller energy scales.

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Surface Structure of Defected CaF₂(111) Layers Studied by Scanned Energy Photoelectron Diffraction

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Electron bombardment on a CaF₂ surface induces the desorption of F and yields metallic Ca, which is oxidized to CaO in the presence of O₂ and/or H₂O [1]. Several investigations on the condition and kinetics of this reaction have been performed, while little is known on the structure of this surface. By chemical-state-resolved X-ray photoelectron diffraction (XPED) measurements, it turned out that CaO grew epitaxially on CaF₂(111) [2]. Scanned energy photoelectron diffraction measurements also elucidated that CaO lattice distortion with 8% lateral expansion occurs parallel to the surface because of the large mismatch [3]. In this study we carried out scanned energy photoelectron diffraction measurements of defected CaF₂ and/or metallic Ca layers induced by electron bombardment, in order to investigate more details of the formation of CaO layers.

Scanned energy photoelectron diffraction measurements have been performed at BL13C in KEK-PF. Samples were prepared by electron bombardment on thin CaF₂ (111) films grown on Ge(111) substrates. The surface structure of this defected and/or metallic layers will be discussed in comparison with those of CaF₂ and CaO layers.

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Initial oxidation features of Si(100) and Si(111) studied by Si 2*p* core-level shift photoemission spectroscopy

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The oxygen adsorption features on the Si(100) and Si(111) surfaces are studied by high-resolution Si 2*p* photoemission measurements. Over the past few years, the initial oxygen absorption on Si surface has been investigated by various experimental techniques[1, 2]. Despite these efforts, the absorption process and reactivity of oxygen on Si surface have been fully understood yet. Precise study of the so-called suboxide (Si^{1+} , Si^{2+} and Si^{3+}) components in Si 2*p* photoemission spectra with high-resolution is needed to elucidate the initial oxidation mechanism.

High-resolution photoemission measurements were performed at the BL-1C of the Photon Factory in KEK, Japan. The samples studied here were grown in situ by exposing clean Si(100) 2X1 and Si(111) 7X7 substrates to dry O₂ gas (2L_22L) at room temperature with changing the absorption time. The spectra were taken with photon energy of 130 eV and 140 eV at a grazing emission angle of 60° from the surface.

The photoemission spectra show that the intensities of each oxidation state are significantly different from those of thermal oxidation. And, from the results of the intensity ratios for the individual oxidation state as a function of O₂ coverage, it is found that the increase for Si^{2+} is the largest for Si(100). For Si(111), however, the increase for Si^{1+} is the largest. Taking into account the surface structure and the existence of bilayer, these aspects in the initial-oxidation process can be explained based on a simple model of oxygen absorption and reaction.

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XPS Study of the Pressure Dependence of the Dry and Wet Oxidation of Germanium Surface

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The oxidation of (011) oriented germanium single crystals has been investigated using X-ray Photoelectron spectroscopy (XPS). In-situ oxidation experiments were carried out at $T=380^{\circ}\text{C}$, under various oxygen partial pressures ranging from 100 mtorr to one atmosphere using a heating cell attached to the electron spectrometer. The surface samples was mechanically and chemically etched prior to the oxidation. The growth kinetics of the oxide layer was monitored by recording O1s, Ge2p and Ge3d XPS lines after successive heat treatments. The oxide layer thickness was estimated by comparing the signal of oxidized and non-oxidized germanium atoms. The results show a strong increase of the growth kinetics of the oxide layers as the partial pressure of oxygen increases. Furthermore, it was observed that the presence of up to 25% water vapor in the atmosphere enhances the growth rate of the oxide layer. These results are used to discuss the oxidation mechanism of germanium surface.

*The authors would like to thank King Fahd University of petroleum and minerals for its support

Structural Properties of Thin CuGaSe₂ Films obtained by EXAFS

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The chalcopyrite semiconductor CuGaSe₂ is a promising material for thin-film solar cells due to its high optical absorption coefficient and the band-gap energy of 1.7 eV at room temperature [1]. To study the optical, electrical and structural properties of the material CuGaS₂GaAs(001), heteroepitaxial layers were grown by metalorganic vapour phase epitaxy (MOVPE). X-ray diffraction (XRD) measurements on epitaxial layers at room temperature revealed strain in the thin layer [1]. Photoluminescence measurements indicate increased strain at lower temperatures. To obtain structural information at low temperatures EXAFS (Extended X-ray Absorption Fine Structure) measurements were performed.

We report on XANES (X-ray Absorption Near Edge Structure) experiments performed at the KMC-2 station at BESSY and EXAFS experiments at the E4 station at HASYLAB. EXAFS spectra were taken for powder material and thin films at the Cu K-edge (8980.5 eV). The XANES measurements were carried out at room temperature and the EXAFS measurements at T = 30 K. Due to the thickness of the sample, measurements in the transmission mode were not possible. Thus a new 4-element-Ge-detector was applied for measurements in fluorescence mode.

The windowless 4-element-Ge-fluorescence detector was placed in the UHV-chamber at an angle perpendicular to the synchrotron radiation. The new feature of the detector is the high counting rate (even for thin films) and the storing of all fluorescence spectra for later analysis. The sample was mounted at a rotatable manipulator. XANES-spectra were collected at different incidence angles. The yields of all 4 Ge-detectors for each angle were added and normalised to the yield of photon electrons measured at an Au-grid or at an ionization chamber. The results indicate an edge shift as a function of the incidence angle.

The EXAFS analysis was performed using the FEFF 7.0 [2] and FEFFIT 3.42 [3] codes. Structural parameters such as the atomic distances R_i and the Debye-Waller factors σ_i^2 with $i = 1, 2, 3$ were extracted. For the Fourier transformed (FT), k-weighted EXAFS oscillation (typical k range 2.5-16 Å⁻¹) a Gaussian window was used. Comparing with the EXAFS results obtained for a powder sample of CuGaSe₂ we found for the 120 nm thin CuGaSe₂ layer an increase of the a-parameter by 0.5% and a decrease of the c-parameter by 1.1%.

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Hydrogen Absorption in Epitaxial W/Nb(001) and Polycrystalline Fe/Nb(110) Multilayers Studied in-situ by EXAFS

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Hydrogen can be absorbed in large quantities by Nb layers of 100 Å thickness embedded in epitaxial W/Nb and polycrystalline Fe/Nb multilayers. The solubility and certain hydrogen-induced structural changes of the host lattice have been previously explored extensively in-situ by means of small-angle neutron/X-ray reflectometry and high-angle diffraction [1]. The reflectometry and diffraction measurements reveal for both systems that the relative out-of-plane expansion of the Nb layers after hydrogen absorption is considerably larger than the relative increase of the Nb interplanar spacing. In polycrystalline Fe/Nb multilayers, hydrogen-induced expansion of interplanar spacing of the Nb layers is a continuous process. In contrast, the Nb lattice expansion in epitaxial W/Nb layers is a discontinuous process, with a structural transition occurring at some hydrogen pressure. For instance, in the case of 60 multilayer stack of [26 Å W/100 Å Nb] at hydrogen pressure of 900 mbar, the maximal increase of the thickness of the layer was 11 %. On the other hand, the interplanar spacing increased by only 6 %. Furthermore, there was observed a structural transition occurring at the hydrogen pressure of 1 mbar.

In order to study the in- and out-of-plane structural changes of epitaxial W/Nb multilayers upon hydrogen absorption in more detail, in-situ Extended X-ray Absorption Fine Structure (EXAFS) experiments have been performed at the RÖMO II station at HASYLAB. Absorption spectra were recorded at the Nb K-edge (18.985 KeV) using the fluorescence detection mode (with a scintillation detector and a 4-element Ge-flourescence detector) at grazing and normal X-ray incidence. From these experiments we obtain selective information about structural changes occurring perpendicular to the layer and within the layer. The samples, which had not been exposed to hydrogen before, were charged from the gas phase at hydrogen pressures ranging from 10⁻⁴ to 900 mbar. The in-situ measurements were carried out at a temperature of T = 185°C. The out-of-plane interplanar structure parameters obtained by EXAFS agree with the results from high-angle X-ray diffraction measurements. Interplanar structure parameters obtained by EXAFS agree with the results from reflectometry and diffraction measurements. We observe by EXAFS also the in-plane expansion of atomic distances (in the case of W/Nb multilayer by about 2.5 %). These results show quantitatively that the total increase of the layer thickness of 11

Scattering mechanism of electrons interacting with surfaces in specular reflection geometry

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It has been recently demonstrated that in the case of HOPG [1], the electron energy loss process in specular reflection geometry is always accompanied by an elastic one. Recent experiments on Ni(110) [2] and Al(100) lead to the same results indicating that the double collision model (DCM) can be considered the dominant scattering mechanism for reflection energy loss spectroscopies (REELS) irrespective of the sample studied and of the transition excited.

From the theoretical point of view the DCM in the REELS was already adopted both in the region of meV and tenth of eV of loss [3] and in the region of hundreds eV of loss [4]. Also from the experimental point of view the DCM is commonly used in the interpretation of EEL experiment but until now a clear experimental evidence for its validity was missing.

The presence of the elastic event in the energy loss processes implies that two independent channels contribute to the inelastic cross section depending on whether the inelastic event precedes (L+D) or follows the elastic one (D+L). Suitable experimental conditions permit to enhance contribution to the cross section of one channel with respect to the other.

The possibility to single out the contribution of a given channel allows to determine without ambiguity the momentum exchanged in the inelastic collision. This is of fundamental relevance for several electron impact spectroscopies, such as EELS and (e,2e), in specular reflection geometry.

These results are derived from measuring the current of elastically and inelastically specularly reflected electrons as a function of the primary electron beam kinetic energy (IV curve). The incident beam energy was varied between 50 and 500 eV, the target was Al(100) and the losses investigated varied between 10 and 35 eV.

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Core Level Photoemission from Strongly Correlated Transition Metal Oxides

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The problem of the correct interpretation of the core-level photoemission spectra of open-shell transition metal (TM) compounds is still an open question. While significant progresses have been recently made on the analysis of core level data of HTSC's and related cuprates [1-4] the analysis of satellites of TM core level spectra in TM compounds (oxides, halides) still needs to be improved and proper calculations addressed. The main reason for this is the rather complicated multiplet structure that may arise from the coupling of the core-hole with the 3d electrons in the outer open shell and the presence of both intra-atomic and inter-atomic screening mechanisms. In addition, other spectral features may arise due to final-state effects, such as plasmon losses and shake-up satellites

Within this frame, it is important to compare the calculation results with photoemission data collected from high quality single crystals with a high energy resolution. Moreover, a consistent identification of the origin of satellite features can provide a reliable reference for computational studies [5] aimed to reproduce the complex spectral features that are found in the experimental data.

X-ray photoemission data from NiO, CoO, FeO, and MnO single crystals are presented and discussed. In particular the 3s and 2s core levels are shown and an analysis of the spectral features is carried out by including exchange splitting, charge transfer satellites, and Coulomb interactions. A cluster calculation of the spectral features is carried out with configuration interaction models and a consistent frame is drawn which allows one to evidence the interplay between exchange splitting and charge transfer energies.

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Inelastic X-ray Scattering as a Novel Tool to Study Mott Insulators.

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The electronic structure of Mott insulators remains a major unsolved problem in physics despite more than half century of intense research efforts. Well-developed momentum-resolved spectroscopies such as photoemission (ARPES) and neutron scattering cannot probe the full Mott gap as ARPES probes the occupied states only and neutron does not couple to the charge channel directly. We report observation of dispersive charge excitations across the Mott gap in a high T_c parent cuprate $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ using high resolution resonant inelastic x-ray scattering performed at the National Synchrotron Light Source (Brookhaven) and Advanced Photon Source (Argonne National Lab). This reveals the anisotropy of full Mott gap in parent cuprate and provides information about the momentum-resolved structure of the upper Hubbard band for the first time. The results are suggestive of an indirect nature of the Mott gap indicating a broken particle-hole symmetry in this parent cuprate. This asymmetry between the occupied Zhang-Rice band (ARPES band) and the unoccupied upper Hubbard band (Inv-ARPES) may provide clues to understand the noted disparity between the p-type and the n-type cuprate superconductors. In this experiment, we demonstrate (1) that given the deeply bulk sensitive, weak coupling nature of this probe and its ability to probe the unoccupied upper Hubbard band and the dynamical charge-charge correlations, inelastic x-ray scattering has the potential to become a powerful probe of complex systems like Mott insulators. In this conference, we plan to discuss how this technique can be used to study dynamical charge correlations in other Mott Insulators like colossal magnetoresistance (CMR) materials (manganites), novel dielectrics stripe-order nickelates etc. (Recent development of a high resolution (diced crystal) Ge analyzer has facilitated such study.)

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The Multidisciplinarity of Spectromicroscopy: Cancer Research, Geomicrobiology, Tribology, Archaeology and Materials Science

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Synchrotron X-ray PhotoElectron Emission Microscopy (X-PEEM) is a useful tool to investigate the microchemical composition of cells in culture as well as thin tissue sections deposited on a conductive substrate. The MEPHISTO X-PEEM, installed at the Wisconsin Synchrotron Radiation Center, after reaching a resolution of 20 nm, has been extensively used for the last four years to investigate a number of systems. Among the most recent results, we will present the micro-localization of gadolinium in glioblastoma cells in culture and tissue sections for cancer neutron capture therapy (NCT). The results prove that gadolinium is preferentially uptaken in the cancer cell nuclei, opening new possibilities for GdNCT clinical trials. Other experiments, exploring the microchemistry of bacteria, rocks, Alzheimer's Disease brain tissue, materials science, tribology and archaeology specimens will be presented. There are different modes of data acquisition that we explored with MEPHISTO, and will discuss: transmission X-PEEM, movie acquisition while scanning the photon energy, X-PEEM of wet samples, how to avoid and/or exploit sample charging.